

Use of the Metals Data File (CRYSTMET) in XAFS analysis

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The X-ray absorption spectrometry (XAS) technique has been widely used to determine the local structure of materials that are poorly suited to study by ordinary diffraction methods, such as fine particles or amorphous matter. XAS is among the major applications at synchrotron radiation facilities and many existing beamlines perform the measurement of XAFS (X-ray absorption fine structure) spectra. XAFS spectra can also be measured with conventional X-ray sources. Measurement of XAFS spectra is relatively straightforward, but real difficulties arise in the analysis and interpretation of the data. Contrary to single-crystal diffraction techniques, the structure is not obtained directly from the measured XAFS data. Model structures must be assumed and the corresponding simulated XAFS spectra must be calculated, with determination of which models best fit the measured data. Model building is a most important part of XAFS analysis, but creation of three-dimensional structures from crystal-chemical considerations can be a very time-consuming task. Utilization of a database of crystal structures and of its built-in structure analysis and display tools can considerably reduce the time and effort required by this task. As XAS is often used to study metals, a database of alloys and intermetallic compounds, such as CRYSTMET, incorporating an array of powerful tools, is then very useful.

1. Introduction

Various methods of investigation of the interatomic bonding in materials are based on the interpretation of measurements of the absorption coefficient, performed with highly monochromatic tunable X-rays. Upon scanning the energy of incident X-rays, the absorbance of the material is, of course, observed to rise sharply at the absorption edges of the constituent elements. In addition, a material-dependent modulation of the absorption coefficient is also observed over a range of 1 to 1000 eV from the edges. This modulation is called X-ray absorption fine structure (XAFS) and the study of this fine structure is called X-ray absorption spectrometry (XAS).

There are two widespread techniques based on XAFS. The first one is called XANES (X-ray absorption near-edge structure) and the other one is called EXAFS (extended X-ray absorption fine structure). XANES focuses on the region that is very close to the absorption edge (usually within ± 50 eV of the energy corresponding to the edge), while EXAFS mostly studies higher energies than XANES. XANES gives information on the electronic states of atoms, while EXAFS gives structural information about short-range order (< 10 Å) in the material. XAFS has been applied to very small particles or to

amorphous materials for which structural information cannot be extracted using *e.g.* X-ray powder diffraction techniques (Koningsberger & Prins, 1988).

The interpretation of EXAFS spectra gives directly the pair distribution function (PDF) of the material. The ensuing analysis of the PDF of a material is based on comparisons with PDFs calculated using three-dimensional structure models. The task of devising such three-dimensional models starting from just crystal-chemical considerations can be time consuming. From this perspective, crystal structure databases can be perceived as collections of crystal-chemically valid three-dimensional models, because the corresponding crystal structures have been observed to exist. It is thus natural to start the model-building procedure by a database search for previously studied chemically analogous materials and then to examine the building blocks of their structures. As many XAFS studies investigate the absorption edge of metal atoms, it is quite appropriate to use for this purpose a database containing mostly alloys and intermetallic compounds, such as CRYSTMET (White *et al.*, 2002).

2. The EXAFS analysis procedure

The ordinary procedure for EXAFS analysis is shown in Fig. 1. It aims at extracting the EXAFS oscillation from the measured raw absorbance data, a process which includes background subtraction and normalization. The extracted EXAFS oscil-

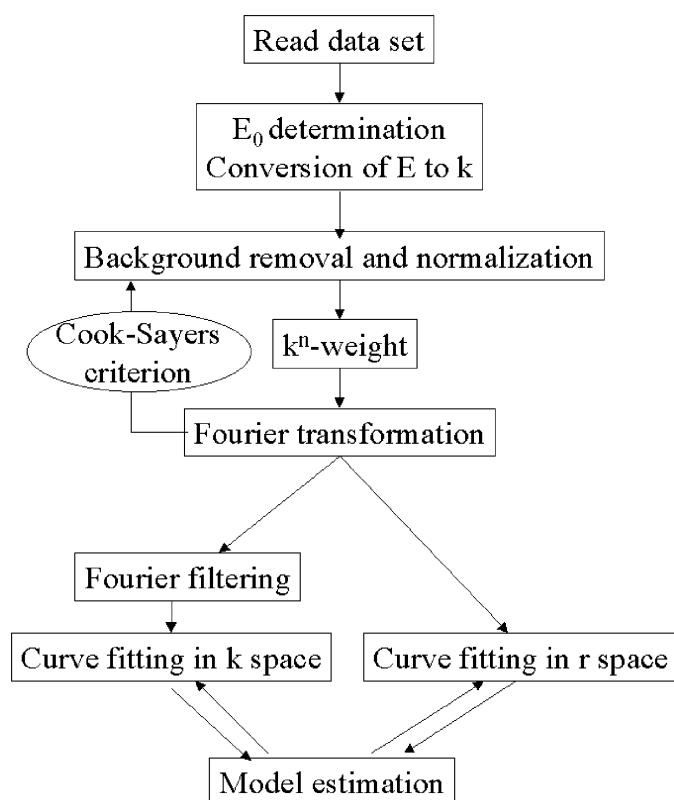


Figure 1
EXAFS analysis procedure.

lation $\chi(k)$ is then Fourier transformed, giving the pair distribution function around the atom at the source of the absorption edge being examined. This pair distribution function may be adjusted in real space directly, or its filtered Fourier transform can be adjusted in reciprocal space, also often called k space. This interpretation of the EXAFS oscillation is commonly performed with the formula

$$\chi_i(k) = \frac{N_i}{kR_i^2} f_i(k) \exp(-2\sigma_i^2 k^2) \exp(-2R_i/\lambda) \sin(2kR_i + \varphi_i),$$

where N is the coordination number, R is the interatomic distance between the absorbing atom and the scattering atom, $f(k)$ is the backscattering amplitude, σ is the Debye–Waller factor, and $\varphi(k)$ is the phase shift. The index i indicates the i th shell of close neighbours (Teo, 1986).

The backscattering amplitudes $f(k)$ and phase shifts $\varphi(k)$ have been calculated, tabulated and published by Teo & Lee (1979) and McKale *et al.* (1988). These theoretical parameters were calculated using a hypothesis of single scattering of the photoelectron by an atom pair. In fact, multiple scattering of the photoelectron should be considered for accurate analyses. Recently developed theoretical calculations, such as *FEFF* (Ankudinov *et al.*, 1998; Rehr *et al.*, 1992; Zabinsky *et al.*, 1995; Ankudinov & Rehr, 1997; Poiarkova & Rehr, 1999), *GNXAS* (Filipponi *et al.*, 1991; Filipponi & Di Cicco, 1995; Filipponi, Di Cicco & Natoli, 1995) and *EXCURVE* (Gurman *et al.*, 1984, 1986; Binsted & Hasnain, 1996), take this multiple scattering into account. Such computer programs calculate the back-scattered amplitude and the phase shift directly from the model structure rather than rely on the above tabulated values. It then becomes possible to calculate model EXAFS spectra using existing crystal structures as a model and then to adjust the model against the observed spectrum. Fig. 2 illustrates an example of such an adjustment between calculated and experimental data (Poiarkova & Rehr, 1999).

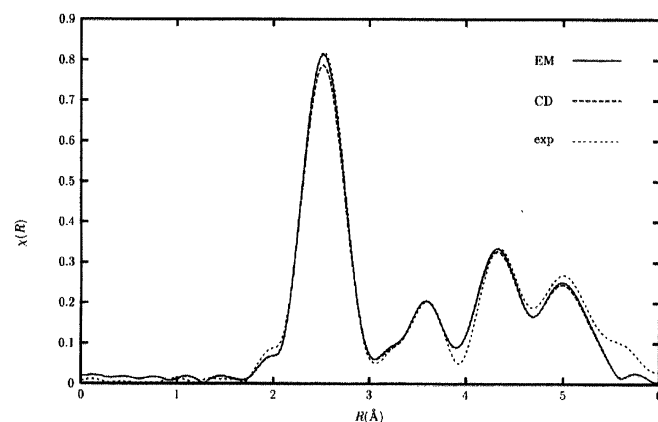


Figure 2
Magnitude of the phase-corrected Fourier transform $\chi(R) = \text{FT}[k\chi(k)]$ for Cu at $T = 150$ K as extracted from experiment using the phase-corrected *FEFFIT* code (short dashed line), and fitted from theoretical results with Debye–Waller factors calculated using the CD (long dashed line) and single force constant EM (solid line) models.

3. Status of databases of XAFS spectra

Databases such as the ICDD, or Toth's *Materials Toolkit* database framework (<http://www.TothCanada.com>), capable of exploiting both ICSD (Belsky *et al.*, 2002) and CRYSTMET (White *et al.*, 2002) structure data, each contain many tens of thousands of searchable experimental or calculated X-ray powder diffraction patterns of known materials. The identification of a material from its experimental powder diffraction spectrum is then routinely performed by searching the stored calculated spectra of known materials for a match of the *d* spacings and intensities of the most intense diffraction lines. XAFS is a relatively new technique and no dedicated database of XAFS spectra is currently available. Some data are available from the International XAFS Society (IXS) Web site (<http://ixs.iit.edu>), but that is still far from being a relational database of XAFS spectra. The creation of an XAFS database is complicated by the following factors. (a) Different beamlines use different data formats. The IXS has created a uniform data submission format, but a database has not yet been created from the submitted entries. (b) The energy resolution depends on both the beamline and the experimental setup. XANES spectra of the same material can then look different, even when recorded on the same sample. Fortunately, EXAFS spectra look more or less the same, especially after Fourier transformation. (c) There is an insufficient number of XAFS setups at synchrotron radiation facilities and few laboratory experimental setups. Given that no practical database of XAFS spectra has yet been created, experimental investigators usually need to prepare a few standard samples of compounds with known structures expected to have similarities with the structure of the unknown sample, but it is sometimes not easy to prepare such samples. Measurements on standard samples are useful for the subtraction of the backscattering amplitude and phase shift. These two parameters are calculated theoretically for each element (*e.g.* Teo & Lee, 1979; McKale *et al.*, 1988) and used for curve fitting, but the use of experimental data extracted from standard samples often gives better fits.

The recent improvement of theoretical calculations (*FEFF*, *GNXAS*, *EXCURVE* *etc.*, as cited above) has enabled the calculation of theoretical XAFS spectra directly from structure models. The fit with experimental data is especially good when multiple scattering is fully taken into account in the calculation.

4. From the XAFS spectrum to the structure of the material

Although EXAFS gives valuable structural information, it may not be the best approach to derive the structure of a totally unknown material. This is because the EXAFS spectrum corresponds to wave propagation along a single direction. The Fourier-transformed oscillation then only gives the pair distribution function. As a result, one can only extract the interatomic distances and coordination numbers. It is possible to identify the chemical nature of the neighbouring atoms, but

without being able to discriminate between elements with adjacent atomic numbers, such as oxygen and nitrogen. It would nevertheless be possible to extract the three-dimensional structure from its EXAFS data. This cannot be performed in a deductive fashion as in single-crystal structure analysis, but one could build several trial models, compute the corresponding EXAFS oscillation, compare it with the experimental spectrum, and in this way obtain the three-dimensional structure by trial-and-error.

Preparation of several standard samples with known structures expected to have similarities with that of the sample has been carried out experimentally and it is probably the best possible method, but it can be difficult to implement in many cases. Fortunately, non-standard analysis of XAFS spectra has recently become possible through state-of-the-art theoretical calculations performed on structure entries in existing crystal structure databases. For simulation, one needs to construct a model. This step can be greatly accelerated through selection of an initial structure in a database. The database function of calculating and displaying the geometry data of structure entries considerably speeds up the screening of search results by comparison with interatomic distances and coordination numbers obtained from the initial analysis of the experimental XAFS spectrum.

5. Aspects of database use for EXAFS purposes

Interatomic distances in a material can be extracted directly by calculations performed on its experimental EXAFS spectrum. In the final analysis, solving the structure of a totally unknown material through unaided interpretation of just its EXAFS spectrum would nevertheless be quite difficult. A model structure is needed in order to perform a good analysis of the EXAFS spectrum. In a way, this process has considerable similarities with Rietveld analysis, but the end result is qualitatively different. Rietveld analysis leads to a refined crystal structure, while EXAFS produces a satisfactory fit with an estimated structure model.

The 'Geometry' tab of the user interface to the CRYSTMET database (White *et al.*, 2002) is very useful for EXAFS analysis, since this function shows interatomic distances and coordination numbers for each independent atom for various shells of neighbouring atoms. Through comparison with the results of a preliminary analysis of the experimental spectrum, one can quickly establish a list of candidates for the model structure, simulate EXAFS spectra and modify parameters. Repetition of this trial-and-error procedure usually converges on a final satisfactory model structure for the material. The 'View Structure' tab displays a crystal-chemically sensible three-dimensional plot of the crystal structure under the interactive control of the user. This visual graphic function helps the user to understand and master the crystal structure. This function is especially useful when metal atoms are distributed over more than one site. The user can usually locate the atom visually through a combination of interactive plots and interactive distance calculations.

6. Examples

6.1. Fe/Co catalyst samples

When an XAFS spectrum of mixtures of metals or alloys displays differences with respect to the superposed spectra of its component phases, then this indicates structural changes in the mixture. Such alloys can, for example, form amorphous materials. The crystal structures of amorphous materials are difficult to determine by X-ray diffraction techniques. In addition, X-ray diffraction methods have difficulties differentiating metals with atomic numbers that are very close. The spectra shown in Fig. 3 (Udagawa, 1993) were measured on two different Fe/Co catalysts supported on silicate. The Fe *K* absorption edge is at *ca* 7.1 keV, while the Co absorption edge is at *ca* 7.7 keV. Comparison of spectra *A* and *B* shows very similar Fe absorption spectra, but different absorption spectra for Co. The conclusion was that Fe and Co exist independently in sample *A*, but the same elements form an alloy in sample *B*. Cobalt, which originally has a face-centred cubic (f.c.c.)

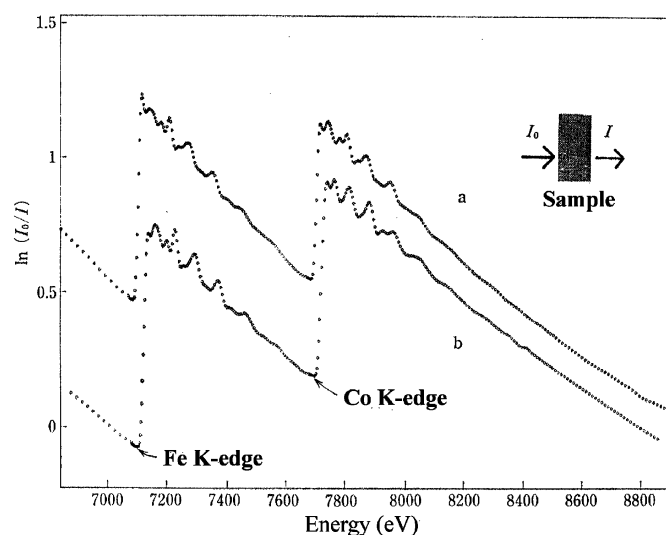


Figure 3
XAFS spectra of an Fe/Co catalyst on silicate.

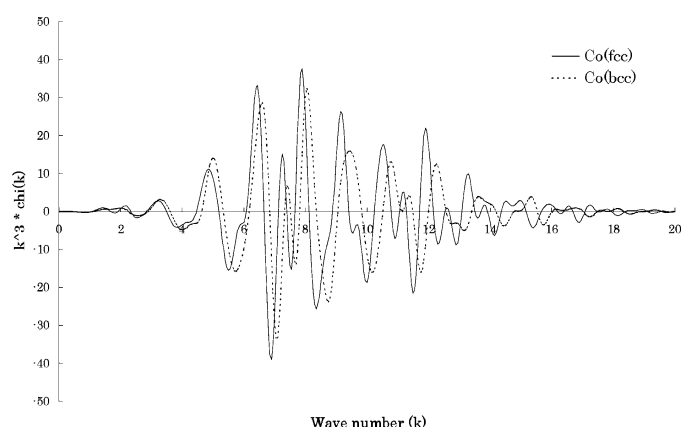


Figure 4
Calculated $k^3\chi(k)$ of face-centred cubic Co and body-centred cubic Co using *FEFF* code.

structure, then substitutes in part for Fe in the body-centred cubic (b.c.c.) lattice of sample *B*. In order to establish this result, the b.c.c. structure of Fe metal was first taken from the database. Half of its Fe atoms were then replaced by Co. Subsequent calculation of a simulated EXAFS spectrum showed good agreement with the measured spectrum. Fig. 4 shows the $\chi(k)$ of f.c.c. Co and b.c.c. Co with k^3 weighting.

Reference materials such as Fe foil and Co foil are easy to obtain for this example, but in many other cases, it can be difficult to obtain good reference samples for the alloy. It is in such cases that the simulation of EXAFS spectra using data from structure database entries realises its full potential in the interpretation of experimental EXAFS spectra. Nevertheless, the database entries can play an important role even in the simpler cases where samples could be procured, as in the present case of Fe/Co alloying.

6.2. Mo oxides on TiO₂

Chun *et al.* (1997) studied the three-dimensional structure of Mo oxides on a TiO₂ substrate by polarization-dependent total-reflection fluorescence XAFS. They deposited

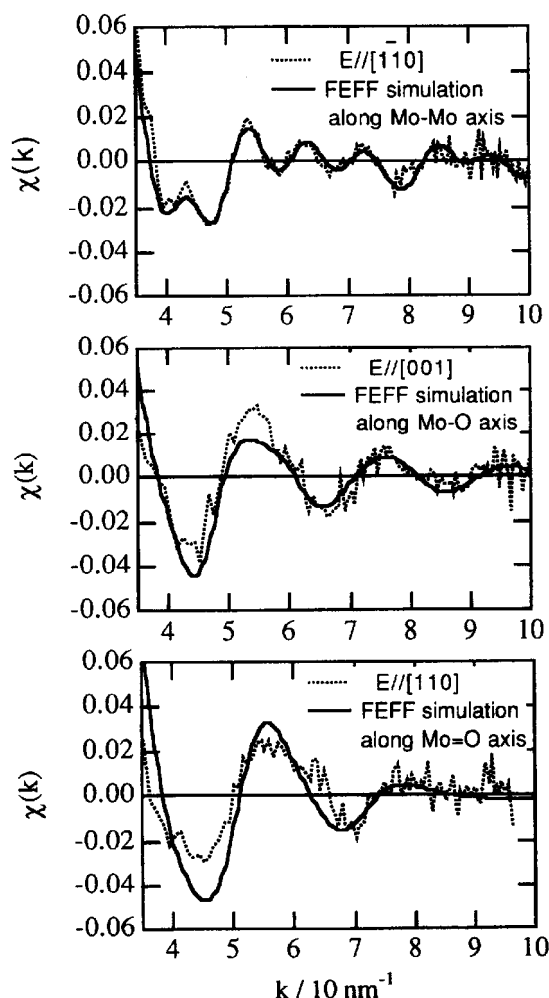


Figure 5
Comparison of Mo *K*-edge polarization-dependent XAFS spectra [Mo oxides on a rutile TiO₂ (110) single crystal] and the *FEFF* simulation.

(NH₄)₆Mo₇O₂₄·4H₂O in ultra-pure aqueous solution onto the (110) face of a single crystal of TiO₂, rutile. That face had been polished to optical standards and annealed in air. After calcination, polarization-dependent total-reflection fluorescence X-ray absorption fine structure (PTRF-XAFS) was measured at the Mo *K* edge. These spectra strongly depend on polarization and are difficult to analyse by regular curve fitting. Construction of a number of models and comparison of their calculated spectra with observed spectra allowed derivation of a satisfactory model of the structure, as shown in Fig. 5.

7. Usage of the database for EXAFS analysis

CRYSTMET-X has an integrated graphical user interface allowing the search of materials based on a number of criteria and the flexible display of search results. The 'Geometry' tab

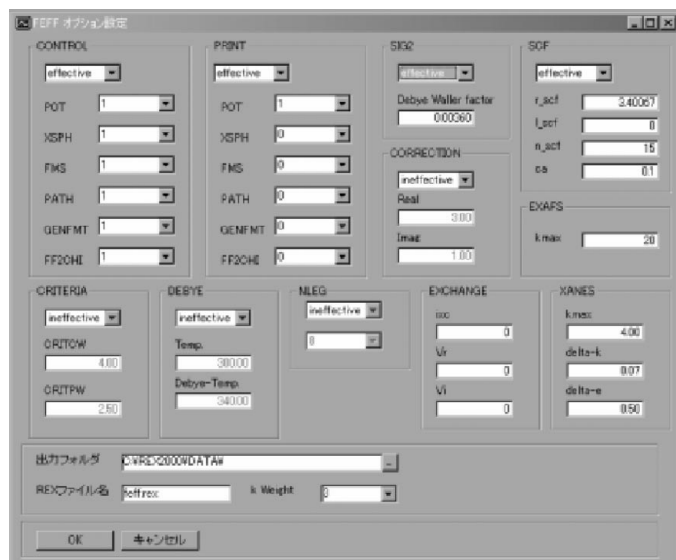


Figure 6
FEFF parameter-setting window (program REX2000).

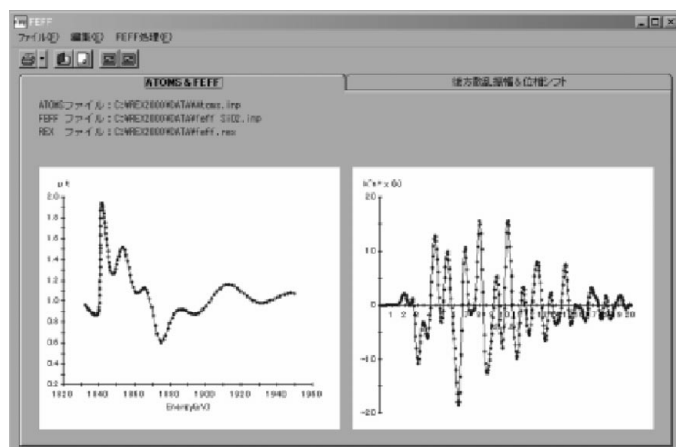


Figure 7
FEFF result plotted on the screen.

shows both a histogram of distances to neighbours and a printout of interatomic distances with coordination numbers up to the desired distance limit. This function gives a good idea of interatomic distances and coordination numbers for the searched materials (Fig. 6). The 'View Structure' tab displays three-dimensional structure plots of materials under the interactive control of the user (Fig. 7). As this flexibility includes, for example, interactive features to slice materials along any desired plane through any point, this constitutes significant assistance in deciding where an atom can be inserted in a structure or deposited on a surface. The recently added 'Atoms' tab is a very useful feature (Fig. 8). This function extracts the information from the database and creates an input file for the program *ATOMS* (Ravel, 2001). *ATOMS* is the program associated with the *FEFF* code. It reads the input file, which contains the crystallographic information, and expands each atom to Cartesian coordinates, so that the *FEFF* code can then calculate the backscattering amplitude and phase shift on this data. The EXAFS analysis package *REX2000* (Rigaku Corp., 2002) constitutes a graphical interface for *FEFF* and *ATOMS*, allowing, for example, the *ATOMS* input file to be read, modified and processed by *FEFF* code. The resulting file, *feff.inp*, can also be modified and several optional parameters can be set (Fig. 6) and processed. The final result is saved and plotted on the screen (Fig. 7). The backscattering amplitude and phase shift can be extracted from the saved data and used for curve fitting of the experimental data.

8. Conclusion

As previously shown, EXAFS analysis can be performed by proposing initial structure models and adjusting them by simulation of EXAFS spectra and comparison with the experimental spectrum until an accurate fit is obtained. This is why the initial model structure is so important and its construction so time-consuming. The use of crystal structure

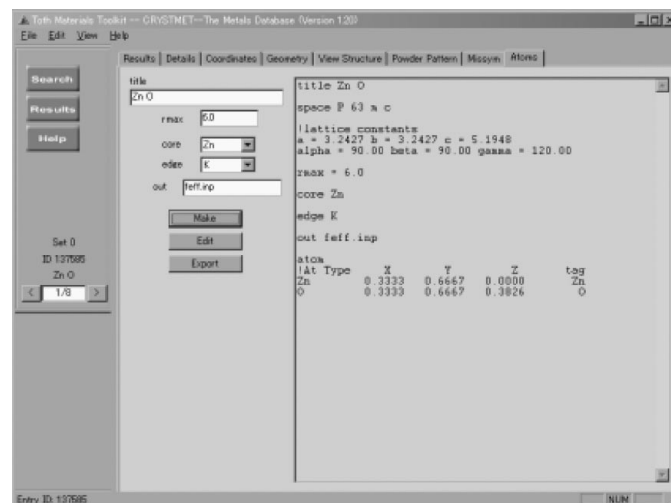


Figure 8
Screen-shot of the 'Atoms' tab.

databases can, therefore, considerably reduce the time spent on this step. Some built-in functions of the CRYSTMET database, such as the distance calculation and the interactive three-dimensional display, actually speed up this process even further.

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